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ABSORPTION SPECTRA OF COBALT-TINTED ALKALI-BORATE GLASSES

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Optical absorption spectra of cobalt-tinted alkali-borate glass in the visible and short IR range (0.4 – 2.7 μm) are studied. An attempt is made to establish a relationship between modifications in the structure of the boron-oxygen lattice and transition of cobalt ions from an octahedral coordination to a tetrahedral one.

Borate glasses in recent decades have remained an object of numerous studies. This interest is due to their structural specifics determined by coordination transformations of boron, which makes borate glass a convenient model system for studying the physicochemical properties of glasses [1].

Our attention was attracted by glasses based on the $R_2O – B_2O_3 – CoO$ systems (where R = Li, Na, K). It is known that Co^{2+} ion imparts a bright blue color to glass. Cobalt in these glasses is present in the form of CoO, which has a strong tinting capacity: 0.1% CoO is sufficient for continuous saturated tinting of glass. We attempted to regard cobalt as an indicator of variations in the coordination state of boron in glass. This approach implied observation of light absorption intensity and shifting of its maximum.

Infrared spectroscopy (IRS) is a simple and informative method for studying the glass structure based on interaction of a material with electromagnetic oscillations of a certain frequency. The IR absorption spectra of crystalline borate material and borate glass within a wavelength range of $600 – 800$ and $1100 – 1500 \ cm^{-1}$ are related to the presence of trigonally coordinated boron, whereas the bands in the range of $990 – 1100 \ cm^{-1}$ are related to the presence of tetrahedrally coordinated boron. The main reason for variations in the coordination of boron is a variation in the content of alkali and alkali-earth metals in glass. With a ratio of $(Me_2O + MeO) : B_2O_3 > 1/3$ conditions are developed for transformation of boron from triangular to a tetrahedral coordination. The shortage of oxygen is compensated at the expense of oxides of alkali and alkali-earth metals [2]. No data were found on coordination of boron and cobalt in alkali-borate glasses changing with a changing temperature.

In our study we made an attempt to identify a relationship between modifications in the structure of the borosilicate lattice and transformation of cobalt ion complexes from the octahedral form into a tetrahedral one in heating up to 500°C based on the absorption spectra of the considered glasses in the short IR-range.

Glasses were melted using reactants of the "chemically pure" grade at 1100 – 1200°C for 50 – 60 min in platinum crucibles. Glass samples were cast in a heated mold and annealed at a temperature of 400°C.

Absorption spectra were measured in glass samples 1.8 – 2.2 mm thick with plane-parallel optically polished surfaces. Absorption spectra were obtained with an SF-4-LSS spectrophotometer designed at the Institute of Chemistry of Silicates of the Russian Academy of Sciences, which makes it possible to register spectra in heating. Monochromatic light within a wavelength range of 0.4 – 2.7 μm was obtained on a monochromator with replaceable grids equipped with replaceable light filters. A quartz halogen lamp was used as a light source. A bolomer served as a receiver. The SF-4-LSS device has a single-channel scheme, whose advantage is simplicity. The error in measuring optical density due to drifting of the lamp luminosity is around ± 1%. Experimental results represent a correlation of optical density with wavelength and temperature $D = f(t, \lambda)$. Dilatometric curves were obtained using a DKV-4 vertical quartz dilatometer.

The viscosity of samples was measured on a viscometer using the method of central bending of a rod within a range from 10^{11} to $10^{13} \ dPa \cdot sec$. The mean quadratic error in this measurement method does not exceed 0.04 of the viscosity logarithm.

Table 1 shows the compositions and properties of the glasses considered. The content of CoO in all glasses is equal and amounts to 0.1% (here and elsewhere molar content is indicated, unless otherwise specified).

It can be seen that the deviation of values determined in synthesis from the values found in analysis does not exceed 1%. The results of measuring the TCLE were used to construct temperature expansion curves for glasses; then an optimum temperature regime of annealing was determined for

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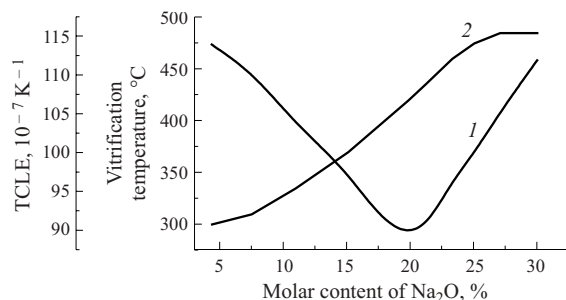
Fig. 1. Dependence of TCLE (*1*) and vitrification temperature (*2*) on Na_2O content.

Fig. 2. Dependence of viscosity logarithm of sodium-borate glasses on temperature. Curve numbers correspond to glass numbers.

each glass considered and its TCLE was calculated (Fig. 1). The results obtained show good agreement with published data [3 – 6].

To describe the temperature dependences of the considered glass within a wide temperature range (Fig. 2) the coefficients in the Vogel – Fulcher – Tamman equation were calculated:

$$\log \eta = A + \frac{B}{T - T_0},$$

where A, B, and T_0 are constants typical of a particular glass.

The values of the constants are shown in Table 2.

Based on the obtained absorption spectra of sodium-borate glasses at room temperature within a wavelength range of 0.4 – 2.7 μm, the presence of several absorption maximums λ_{max} was registered: in ranges of 0.4 – 0.7 and 0.7 – 2.5 μm, which are typical of all compositions. An increased content of alkali components in glass leads to a perceptible increase in the intensity of absorption bands in the visible spectrum range and modifies its shape. Thus, glass with 4.3% Na_2O has two weakly expressed maximums at $\lambda_{max} = 0.51$ and 0.55 μm with respective intensities $K_{max} = 1.12$ and 1.29 cm^{-1} (Table 3) and glass containing

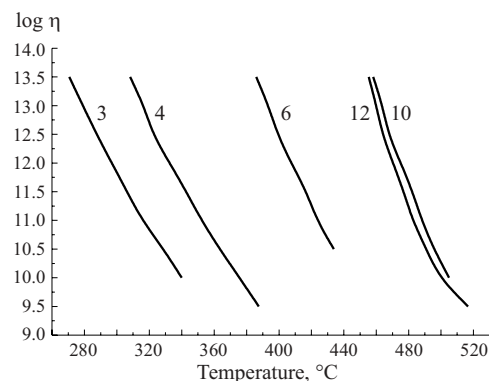over 23.3% R_2O has a clearly expressed triplet with bands at 0.52, 0.59, and 0.63 μm and $K_{max} = 2.65$, 3.86, and 3.88 cm^{-1}. Furthermore, an increased content of R_2O causes a shift of λ_{max} to the long-wave range.

Comparing absorption in glasses that have equal quantities of the alkaline component (around 10% found in analysis) but different cations (R = Li, Na, K), it can be seen that these glasses within the considered wavelength range have different intensities; they decrease in the following order: Li > Na > K.

The absorption spectra of the sodium-borate glass series in an interval of 0.7 – 2.5 μm clearly exhibit an absorption band with a maximum of 1.4 μm in glasses with an alkali content up to 21.18%. Furthermore, a modification of its shape is observed: widening of the band with the maximum of 1.4 μm and the second peak with $\lambda_{max} = 1.6$ μm.

Several peaks with $\lambda_{max} = 2.0$, 2.15, and 2.4 μm are discovered, whose intensity decreases with increasing alkali content, and the peaks with $\lambda_{max} = 2.15$ and 2.4 μm drop from 2.069 to 1.481 cm^{-1} and from 3.474 to 1.844 cm^{-1}, respectively.

TABLE 1

Glass	Alkali component	Alkali component content, %				TCLE, 10^{-7} K^{-1}	Vitrification temperature, °C	Visual characteristics
		from synthesis		from analysis				
		mass	molar	mass	molar			
1	Li_2O	4.55	10.00	4.61	10.16	95	350	Clear, light lilac
2	K_2O	12.90	10.00	12.80	9.84	110	310	The same
3	Na_2O	3.11	3.50	3.83	4.30	114	300	Clear, pale pink
4	Na_2O	6.25	7.00	6.69	7.50	110	310	Clear, pink
5	Na_2O	8.96	10.00	9.94	10.96	104	335	Clear, light lilac
6	Na_2O	13.50	15.00	13.62	15.11	97	370	Clear, lilac
7	Na_2O	16.28	18.00	17.99	19.84	90	420	Clear, lilac with a violet shade
8	Na_2O	19.06	21.00	19.21	21.18	91	435	Clear, blue-violet
9	Na_2O	20.92	23.00	21.19	23.30	96	460	Clear, blue
10	Na_2O	22.79	25.00	22.81	25.02	100	475	The same
11	Na_2O	24.67	27.00	24.71	27.06	105	485	Clear, dark blue
12	Na_2O	27.51	30.00	27.60	30.08	112	482	The same

Glasses containing alkaline cations with opposite signs have absorption spectra curves of similar shapes and positions of bands and differ only in their intensity.

Absorption maximums related to the presence of CoO are registered in the spectra of the considered glasses in a wavelength range of 0.4 – 0.7 µm. With low concentrations of alkali oxides, the absorption band has two maximums, 0.51 and 0.55 µm, which determines the pink color of the glass. According to contemporary notions, octahedral cobalt prevails in these glass compositions (1 – 4) and exists in a matrix, in which boron has a triple environment. As glass becomes saturated with R_2O, a third maximum with $\lambda_{max} = 0.62$ µm emerges. The presence of three absorption maxima indicates that cobalt ions in glasses exist in two coordination states: six and four. As the content of alkaline oxides increases, the equilibrium between octahedral cobalt ($\lambda_{max} = 0.51$ µm) and tetrahedral cobalt ($\lambda_{max} = 0.59$ and 0.63 µm) shifts toward the latter. This change in the ratio between the bands produces a modification in glass tinting. With the formation of a band with $\lambda_{max} = 0.63$ µm, glasses primarily acquire a blue tint and then with an increasing difference in intensities at wavelengths of 0.51 and 0.55 µm the glasses become bright blue. Transformation of boron from three to four coordination is accompanied by intensification of the blue color in the glass.

Glasses with a low content of R_2O (glasses 1 – 4, 6, 7) have an absorption band with a maximum $\lambda_{max} = 1.4$ µm in the IR range, which presumably relates to a valence vibration overtone of the $B – OH$ group in fixed water. With an increasing content of alkaline component the intensity of this band decreases. With a further increase in the R_2O content in glass a group of wide overlapping bands emerges in this range with maximums at 1.2, 1.4, and 1.6 µm. These bands most probably relate to coordination-unsaturated cobalt ion (in blue glasses). The intensity of three other bands with maximums at $\lambda_{max} = 2.0$, 2.15, and 2.4 µm also decreases with increasing content of alkali oxides. Most probably they also relate to valence vibration overtones of groups $B – OH$.

We registered temperature variations in the absorption spectra of glasses 3 and 10 (Table 1) in a wavelength interval from 0.4 to 2.7 µm.

The general course of the temperature dependence of the absorption coefficient on wavelength for glass 3 reveals that its heat-

ing from room temperature to 330°C raises the absorption coefficient within the entire spectrum range considered without changing the shape of the curve and without shifting the

TABLE 2

Glass	Coefficient		
	A	B	T_0
3	– 3.00	4282.3	284.2
4	– 3.00	4150.0	329.8
6	– 3.00	3554.6	445.3
10	– 2.86	2748.8	565.3
12	– 3.00	2677.8	567.6

TABLE 3

Glass	Range 0.4 – 0.7 µm				Range 0.7 – 2.7 µm			
	λ_{max}	K_{max}	$K_{0.8}$	$K_{max} - K_{0.8}$	λ_{max}	K_{max}	$K_{1.8}$	$K_{max} - K_{1.8}$
1	0.51	1.847	0.840	1.007	1.40	1.077	0.855	0.192
	0.55	2.125		1.285	2.15	2.285		1.400
					3.574			2.719
2	0.51	1.106	0.244	0.862	1.40	0.485	0.255	0.260
	0.55	1.171		0.927	2.15	1.405		1.180
					2.30	–		–
					2.40	1.624		1.399
3	0.51	1.118	0.294	0.824	1.40	0.606	0.377	0.229
	0.55	1.292		0.998	2.00	0.714		0.337
					2.15	1.974		1.597
					2.40	3.369		3.313
4	0.51	1.520	0.788	0.732	1.40	0.984	0.593	0.391
	0.55	1.542		0.754	2.05	1.093		0.500
					2.20	2.466		1.873
					2.40	3.943		3.350
5	0.52	1.788	0.434	1.354	1.40	0.755	0.506	0.249
	0.55	1.806		1.372	2.00	0.753		0.247
					2.15	2.069		1.563
					2.40	3.474		2.968
7	0.51	1.831	0.258	1.573	1.40	0.532	0.430	0.102
	0.57	2.306		2.048	2.00	–		–
	0.62	1.937		1.679	2.15	0.900		0.470
					2.40	1.761		1.331
8	0.51	1.955	0.205	1.750	1.40	0.572	0.454	0.118
	0.57	2.501		2.296	2.00	–		–
	0.62	2.229		2.024	2.15	0.838		0.384
					2.40	1.627		1.173
9	0.51	2.654	0.241	2.413	1.40	0.891	0.716	0.175
	0.57	3.857		3.616	1.60	0.816		0.100
	0.62	3.882		3.641	2.15	1.106		0.390
					2.40	1.844		1.128
10	0.52	3.733	0.328	3.405	1.40	1.108	0.948	0.160
	0.59	5.474		5.146	1.60	1.084		1.136
	0.63	5.592		5.264	2.15	0.908		0.040
					2.40	–		
11	0.52	0.575	0.328	0.247	1.40	1.317	1.715	0.398
	0.59	6.769		6.441	1.60	1.275		0.440
	0.63	6.894		6.566	2.15	1.002		0.713
					2.40	–		–
12	0.52	6.252	0.698	5.544	1.40	2.089	1.062	1.027
	0.59	9.276		8.578	1.60	2.014		0.952
	0.63	8.990		8.292	2.15	1.481		0.419
					2.40	–		–

maximum. There is an obvious increase in the intensity of the absorption band with $\lambda_{max} = 0.55$ µm with increasing temperature. The interval of $0.7 - 2.6$ µm exhibits four bands, whose intensities and absorption maximums coincide in their positions with the spectra registered at room temperature in glass 3. As the temperature increases, the intensities of all bands grow.

Heating glass 3 containing 3.83% Na_2O does not lead to transition of cobalt ions from the octahedral coordination into a tetrahedral one; however, increased intensity of absorption may indicate an increased concentration of groups with six-coordination cobalt.

The main transformations of glass 10 are registered in a wavelength range of $0.4 - 0.7$ µm. The absorption band at a wavelength of 0.51 µm does not change under heating to a temperature of 450°C, and the intensity of bands with $\lambda_{max} = 0.59$ and 0.63 µm decreases; however, these bands grow wider and their maximum is shifted to the long-wave spectrum range.

The absorption spectra of glass 10 containing 25.02% Na_2O undergo transformations in a temperature range of $20 - 450$°C. The absorption band with $\lambda_{max} = 0.51$ µm correlates with a saturated coordination state of cobalt and heating of glass does not cause its modification (in contrast to glass 3). This absence of change may speak of the stability of six-coordination cobalt with increasing temperature.

A decrease in the intensity of absorption bands with $\lambda_{max} = 0.59$ and 0.63 µm and widening of absorption bands may be related to a distortion of tetrahedrons, which increases the number of possible states of Co^{2+} complex.

The general growth of intensities of bands belonging to overtones of hydroxyl groups ($0.8 - 2.4$ µm) is not substan-

tial and may be due to a temperature shift of the long-wave absorption edge in glass.

Thus, in studying glasses containing around 10% alkali oxides it has been established that the absorption coefficient of lithium glass is higher than that of sodium and potassium glass and the positions of maximums virtually coincide. The maximum in the sodium series glasses with an increasing alkali content under a wavelength of $0.4 - 0.7$ µm is shifted toward the long-wave range. Modification of the shape and intensities of absorption bands is expressed most clearly in the interval $0.4 - 2.7$ µm. Cobalt ions in all glasses exist in a bivalent state. As the Na_2O content in glass increases, cobalt transforms from a six-coordination to a four-coordination state and boron from a three-coordination to a four-coordination state. These transformations are accompanied by changing of the glass color from pink to a dark blue.

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